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(54) **METHOD FOR PRODUCING BINDER PITCH**

(57) A method for producing a binder pitch for a carbon material, comprising heat-treating a petroleum-based heavy oil (step 1); distilling the heat-treated product obtained in step 1 to obtain a base pitch having a softening point of 60°C or more and 110°C or less, a fixed carbon content of 50.0% by mass or more, an initial

boiling point of 320°C or more and 450°C or less, and a quinoline insoluble matter (QI) of 1.0% by mass or less as a high boiling point component (step 2); adding carbon powder to the base pitch obtained in step 2 and mixing them (step 3).

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Description

TECHNICAL FIELD

[0001] The present disclosure relates to a method for producing a binder pitch for a carbon material, such as a graphite electrode.

BACKGROUND

[0002] Carbon materials, such as a graphite electrode used in an electric furnace for remelting iron are produced by kneading and forming aggregates, such as coke, and pitch (referred to as "binder pitch") at a temperature equal to or higher than the softening point of the binder pitch, followed by baking, and then graphitizing. Since it is necessary that the carbon material have properties such as high mechanical strength, high electrical conductivity, and high thermal conductivity, the carbon material preferably has high density. However, the baked body has a structure having a large number of pores due to volatilization of low-molecular-weight components in the binder pitch during the baking step, etc. Therefore, in the production process, impregnating the baked body with pitch (referred to as "impregnation pitch") followed by re-baking several times reduces the porosity and results in the obtained carbon material having high density.

[0003] Heavy residue oil (ethylene bottom oil), which is a by-product when producing olefins, such as ethylene and propylene by steam cracking or thermal cracking of petroleum hydrocarbons, such as naphtha, is used only partially as a raw material for carbon black, and mostly as a fuel. Therefore, converting this ethylene bottom oil into high value-added products is an object in the relevant technical field. In order to achieve this object, attempts have been made to produce a binder pitch for carbon materials from ethylene bottom oil, taking advantage of the characteristics of ethylene bottom oil, which contains large amounts of aromatic compounds. However, a petroleum-based pitch produced from petroleum-based heavy oil, such as ethylene bottom oil, has a lower carbon yield than a coal tar pitch having the same softening point as the petroleum-based pitch, and thus the density of the obtained carbon material tends to be lower. Therefore, petroleum-based pitches are currently not used very often.

[0004] Some of the most important properties required for the binder pitch are carbon yield, softening point, and initial boiling point. The higher the carbon yield, the more the density of the obtained baked body, which is preferable, since the number of subsequent impregnations with the impregnation pitch and re-baking can be reduced. When the softening point is too high, the kneadability and the formability are lowered, and therefore the softening point is preferably about 120°C or less. When the initial boiling point is too low, the amount of light components volatilized during kneading is large, so that the viscosity increases during kneading, and the kneadability and the formability are lowered. Therefore, the initial boiling point is preferably about 320°C or more. In general, as a method of increasing the carbon yield and the initial boiling point of the binder pitch, there is a method of removing light components in the pitch by distillation, etc. However, the method has a problem in that the softening point also increases when the light components are removed.

[0005] As a method of improving the carbon yield while suppressing an increase in the softening point to some extent, there is a method of adding a cutback oil pitch having a relatively high carbon yield and a high softening point (Patent Literature 1).

[Citation List]

[Patent Literature]

[0006] [PTL 1] US 6352637 B2

SUMMARY OF INVENTION

[Technical Problem]

[0007] The method described in Patent Literature 1 has a problem that the initial boiling point of the obtained pitch is lowered, since it is necessary to add a cut-back oil having a relatively low boiling point. Thus, it is difficult to adjust these parameters independently using conventional methods.

[0008] The present disclosure provides a method for producing pitch suitable for a binder pitch for a carbon material from petroleum-based heavy oil, wherein the pitch has a high carbon yield and excellent kneading stability.

[Solution to Problem]

[0009] The present inventors have conducted intensive studies to obtain an excellent binder pitch for carbon materials

from petroleum-based heavy oil. As a result, the present inventors have found that pitch suitable for a binder pitch for carbon materials can be obtained by adding carbon powder to a base pitch having a high fixed carbon content, a high initial boiling point, and a low softening point, which is obtained by heat-treating petroleum-based heavy oil and then distilling it, and mixing them, thereby completing the present invention.

[0010] That is, the contents of the present disclosure relate to the following methods [1] to [7].
[0011]

[1] A method for producing a binder pitch for a carbon material, comprising heat-treating a petroleum-based heavy oil (step 1);

distilling the heat-treated product obtained in step 1 to obtain a base pitch having a softening point of 60°C or more and 110°C or less, a fixed carbon content of 50.0% by mass or more, an initial boiling point of 320°C or more and 450°C or less, and a quinoline insoluble matter (QI) of 1.0% by mass or less as a high boiling point component (step 2);

adding carbon powder to the base pitch obtained in step 2 and mixing them (step 3).

[2] The method for producing a binder pitch for a carbon material according to [1], wherein a 3% distillation temperature of the base pitch is 340°C or more and 470°C or less.

[3] The method for producing a binder pitch for a carbon material according to [1] or [2], wherein the petroleum-based heavy oil is an ethylene bottom oil light fraction.

[4] The method for producing a binder pitch for a carbon material according to any one of [1] to [3], wherein the carbon powder is at least one selected from the group consisting of graphite powder, coke powder, carbon black powder, and free carbon powder in coal tar.

[5] The method for producing a binder pitch for a carbon material according to any one of [1] to [4], wherein an amount of the carbon powder added is 1.0 parts by mass or more and 22.0 parts by mass or less with respect to 100 parts by mass of the base pitch.

[6] The method for producing a binder pitch for a carbon material according to any one of [1] to [5], wherein the binder pitch for a carbon material obtained in step 3 has a softening point of 80°C or more and 120°C or less, and a quinoline insoluble matter of 18.0% by mass or less.

[7] The method for producing a binder pitch for a carbon material according to any one of [1] to [6], wherein the carbon material is a graphite electrode.

[Advantageous Effects of Invention]

[0012] According to the present disclosure, pitch suitable for a binder pitch for a carbon material from petroleum-based heavy oil can be obtained. Specifically, it is possible to obtain a binder pitch having a high carbon yield and excellent kneading stability for a carbon material. By using this binder pitch for the production of a carbon material, a high density carbon material can be obtained.

BRIEF DESCRIPTION OF DRAWINGS

[0013]

FIG. 1 is a flow chart showing a petrochemical process for thermal cracking of naphtha, etc., and a method for producing ethylene bottom oil.

FIG. 2 is a diagram showing the change with time in the viscosity increase rate at 170°C of various pastes (kneaded product of needle coke and various binder pitches, needle coke:binder pitch = 3:7 (mass ratio)).

DESCRIPTION OF EMBODIMENTS

[0014] Hereinafter, preferred embodiments of the present invention will be described, but it should be understood that the present invention is not limited to these embodiments only, and various applications can be made within the spirit and practice of the present invention.

[0015] In the present specification, when using "to" for a numerical range, the numerical values at both ends are the upper limit value and the lower limit value, respectively, and are included in the numerical range. Values of softening point, fixed carbon content, quinoline insoluble matter, initial boiling point, etc., are determined by the methods described in the Examples section.

<Method for producing binder pitch>

[0016] The method for producing a binder pitch of one embodiment comprises at least the following steps 1 to 3 in this order, and may comprise other steps.

Step 1 (heat treatment step): heat-treating a petroleum-based heavy oil

Step 2 (distillation step): distilling the heat-treated product obtained in step 1 to obtain a base pitch having a softening point of 60°C or more and 110°C or less, a fixed carbon content of 50.0% by mass or more, an initial boiling point of 320°C or more and 450°C or less, and a quinoline insoluble matter (QI) of 1.0% by mass or less as a high boiling point component

Step 3 (carbon powder mixing step): adding carbon powder to the base pitch obtained in step 2 and mixing them to obtain a binder pitch

[0017] The petroleum-based heavy oil used as a raw material is not particularly limited as long as it can provide a base pitch having desired characteristics in step 2, but preferably has the following composition. That is, the content of a fraction having a boiling point of less than 150°C in the petroleum-based heavy oil is preferably 5% by mass or less, more preferably 2% by mass or less, and still more preferably 1% by mass or less. The content of a fraction having a boiling point of 150°C or more and less than 450°C in the petroleum-based heavy oil is preferably 75% by mass or more, more preferably 85% by mass or more, and still more preferably 90% by mass or more. The content of a fraction having a boiling point of 450°C or more and less than 550°C in the petroleum-based heavy oil is preferably 15% by mass or less, more preferably 10% by mass or less, and still more preferably 8% by mass or less. The content of a fraction having a boiling point of 550°C or more in the petroleum-based heavy oil is preferably 5% by mass or less, more preferably 3% by mass or less, and still more preferably 1% by mass or less. The content of a fraction in each temperature range refers to a percent recovered in each temperature range when a distillation curve of the petroleum-based heavy oil is determined. The distillation curve can be determined by selecting a suitable calculation method from JIS K 2254:2018, ASTM D7500-15 and ASTM D7169-16 according to the type of the petroleum-based heavy oil, and carrying out a measurement.

[0018] Examples of the petroleum-based heavy oil having the aforementioned composition include an ethylene bottom oil light fraction. In the petrochemical industry, in general, naphtha and the like are thermally cracked at a high temperature, and the obtained thermally cracked product is distilled and separated into fractions of ethylene, propylene, and other olefins; aromatic compounds, such as benzene, toluene, and xylene; cracked gasoline, cracked kerosene, etc., to obtain products. Among these fractions, a heavy fraction having the highest boiling point is referred to as ethylene bottom oil, which is used in a raw material of carbon black, etc., and as a fuel (see FIG. 1). Since a thermal cracking plant for naphtha and the like is often referred to as an ethylene plant, the aforementioned heavy fraction is referred to as ethylene bottom oil.

[0019] Although the properties of ethylene bottom oil obtained by thermal cracking of naphtha-containing raw materials depend on the type of naphtha-containing raw material, thermal cracking conditions, operating conditions of the refining distillation tower, etc., the general properties are that the 50% distillation temperature is 200°C to 400°C, the aromatic carbon content is 50% by mass or more, the flash point is 70°C to 100°C, and the 50°C kinematic viscosity is less than 40 mm²/s. However, since the ethylene bottom oil is a mixture of hydrocarbons, the above values may vary to some extent.

[0020] The ethylene bottom oil light fraction refers to a distillate obtained by distilling off an arbitrary ratio (for example, 5% by mass to 70% by mass) of light components from ethylene bottom oil by a distillation operation, etc. The high boiling point component obtained at this time is referred to as an ethylene bottom oil heavy fraction. Ethylene bottom oil, an ethylene bottom oil heavy fraction, or other heavy oil may be added to the ethylene bottom oil light fraction as long as it falls within the above preferable composition. Examples of other heavy oil include, but are not limited to, fluid catalytic cracking oil (FCC decant oil), normal pressure distillation residue oil, vacuum distillation residue oil, hydrotreated petroleum-based heavy oil, cracked kerosene, and coal tar. The sulfur content and nitrogen content of the pitch are preferably as small as possible because they cause puffing during baking. When a graphite electrode is produced using pitch containing a large amount of metal components, these metal components evaporate during graphitization, reducing the density of the graphite electrode, which may be undesirable in terms of product quality. From these points of view, other heavy oil is preferably low in sulfur content, nitrogen content, and metal component. Fluid catalytic cracking oil (FCC decant oil) and cracked kerosene are preferable as such other heavy oil. Although the properties of fluid catalytic cracking oil (FCC decant oil) depend on the raw materials and operating conditions, the general properties are that the 50% distillation temperature is 300°C to 450°C, the flash point is 60°C to 160°C, and the 40°C kinematic viscosity is less than 40 mm²/s at 40°C. However, since fluid catalytic cracking oil (FCC decant oil) is a complex mixture, the above values may vary to some extent. In one embodiment, the petroleum-based heavy oil is an ethylene bottom oil light fraction.

[0021] Cracked kerosene is a mixture composed mainly of hydrocarbons having 9 or more carbon atoms and produced in petrochemical processes, and is a fraction having a boiling point in the range of 90°C to 230°C at 1 atm. However, since cracked kerosene is a mixture of hydrocarbons, the number of carbon atoms and boiling point may vary to some extent.

[0022] Examples of primary components of cracked kerosene include xylene, styrene, allylbenzene, propylbenzene,

methylethylbenzene, trimethylbenzene, methylstyrene, dicyclopentadiene, indane, indene, methylpropylbenzene, methylpropenylbenzene, ethylstyrene, divinylbenzene, methylindene, naphthalene, and methyldicyclopentadiene.

(Step 1: Heat treatment step)

[0023] Step 1 is a step of heat-treating a petroleum-based heavy oil. The heat treatment is preferably carried out under a non-oxidizing gas atmosphere in a sealed vessel. Examples of the non-oxidizing gas include nitrogen gas, argon, hydrogen gas, lower alkanes, such as methane and ethane, and a mixed gas of these non-oxidizing gases. Nitrogen gas is preferable from the viewpoint of cost and ease of handling.

[0024] The heat treatment temperature is preferably 380°C or more, more preferably 400°C or more, and still more preferably 410°C or more. The heat treatment temperature is preferably 500°C or less, more preferably 480°C or less, and still more preferably 450°C or less. The upper limit values and the lower limit values can be arbitrarily combined. The preferable range is 380°C to 500°C, more preferably 400°C to 480°C, and still more preferably 410°C to 450°C.

[0025] Appropriate heat treatment time depends on the heat treatment temperature. When the heat treatment temperature is 380°C to 400°C, it is preferably 3 hours to 48 hours, and more preferably 6 to 48 hours, from the time when the predetermined heat treatment temperature is reached (the same applies hereinafter). When the heat treatment temperature is more than 400°C and 430°C or less, it is preferably 1 hour to 24 hours, and more preferably 3 hours to 16 hours. When the heat treatment temperature is more than 430°C and 500°C or less, it is preferably 0.1 hours to 16 hours, and more preferably 0.5 hours to 8 hours. The upper limit values and the lower limit values of the appropriate heat treatment time in each heat treatment temperature condition can be arbitrarily combined.

[0026] By heat-treating a petroleum-based heavy oil having the aforementioned preferable composition under the conditions satisfying the aforementioned heat treatment temperature and heat treatment time, a base pitch having particularly suitable physical properties for producing carbon materials, such as a graphite electrode can be obtained. This base pitch can be used as a binder pitch and an impregnation pitch in the production of carbon materials, such as a graphite electrode.

[0027] The pressure at the beginning of heat treatment (initial pressure) is preferably 0 MPaG, but is not particularly limited. The pressure in the sealed vessel is increased by hydrogen, and lower alkanes, such as methane and ethane, generated by thermal decomposition during the heat treatment. There is no limitation on the pressure inside the sealed vessel, which may be reduced as necessary. However, the heat treatment is preferably carried out under pressure since yield of the base pitch obtained in step 2 tends to increase. When the heat treatment is carried out under pressure, the pressure range is preferably, for example, about 0.1 MPaG to 15 MPaG.

[0028] As described in JP S60-179493 A and JP S60-240790 A, an additive, such as a solid catalyst may be added during the heat treatment of petroleum-based heavy oil, but in this case, it is necessary to add a step of removing the additive before step 3.

(Step 2: Distillation step)

[0029] Step 2 is a step of removing low boiling point components by distilling the heat-treated product obtained in step 1 to obtain pitch having desired characteristics as a high boiling point component. The pitch having the desired characteristics is referred to as a "base pitch". The distillation method in step 2 may be any of atmospheric distillation, reduced-pressure distillation (vacuum distillation), or a combination of atmospheric distillation and reduced-pressure distillation, and can be appropriately selected. It is preferable that the internal temperature of a distillation apparatus does not exceed 360°C. This is because, when the temperature exceeds 360°C, a reaction, such as polymerization is more likely to occur and coking may occur on the inner wall of the distillation apparatus. The lower limit temperature does not affect the properties of the pitch, but is preferably 200°C or more in terms of economic efficiency, since, when the temperature is low, the distillation pressure must be reduced in order to distill off low boiling point components. When carrying out reduced-pressure distillation (vacuum distillation), the pressure during distillation is preferably 100 PaA to 10,000 PaA, more preferably 500 PaA to 3,000 PaA, and still more preferably 800 PaA to 2,000 PaA in order to obtain a base pitch having an initial boiling point of 320°C or more. In general, the higher the distillation end point, the higher the initial boiling point. In order to set the initial boiling point of the obtained base pitch to 320°C or more, and the 3% distillation temperature of that to 340°C or more, the distillation end point in terms of normal pressure is preferably 320°C or more, and more preferably 330°C or more, although it depends on the type of petroleum-based heavy oil used, the heat treatment conditions in step 1, and the distillation conditions in step 2, etc.

[0030] The softening point of the base pitch obtained in step 2 of one embodiment is 60°C or more, and more preferably 70°C or more. The softening point of the base pitch obtained in step 2 of one embodiment is 110°C or less, and more preferably 100°C or less. The upper limit values and the lower limit values can be arbitrarily combined. The preferable range is 60°C or more and 110°C or less, and more preferably 70°C or more and 100°C or less. When the softening point is 60°C or more and 110°C or less, the softening point of the obtained binder pitch is 80°C or more and 120°C or less, which is

preferable, although it depends on the type and amount of the carbon powder, which is added and mixed in step 3. The softening point is determined by the method described in the Examples section.

[0031] Since the carbon yield tends to increase as the fixed carbon content increases, the fixed carbon content of the base pitch of one embodiment is 50.0% by mass or more, and more preferably 51.0% by mass or more. The upper limit of the fixed carbon amount is not particularly limited, but is, for example, 75.0% by mass or 85.0% by mass. The fixed carbon content is determined by the method described in the Example section.

[0032] The initial boiling point of the base pitch of one embodiment is 320°C or more, and more preferably 350°C or more. The initial boiling point of the base pitch of one embodiment is 450°C or less, and more preferably 400°C or less. The upper limit values and the lower limit values can be arbitrarily combined. The preferable range is 320°C or more and 450°C or less, and more preferably 350°C or more and 400°C or less. When the initial boiling point is 320°C or more, the amount of light components volatilized at a kneading temperature (for example, 140°C to 180°C) is small, so that the viscosity of the pitch during kneading hardly increases, and kneading can be carried out well. On the other hand, when the initial boiling point exceeds 450°C, the softening point of the base pitch may exceed 110°C, although it depends on the raw material and heat treatment conditions of step 1. Therefore, the initial boiling point is preferably 450°C or less. The initial boiling point is determined by the method described in the Examples section.

[0033] The quinoline insoluble matter (QI) of the base pitch of one embodiment is 1.0% by mass or less, more preferably 0.5% by mass or less, and still more preferably 0.1% by mass or less. When the QI of the base pitch is 1.0% by mass or less, the binder pitch obtained has a QI of 18.0% by mass or less, which is preferable, although it depends on the type and amount of the carbon powder, which is added and mixed in step 3. The lower limit of QI of the base pitch is not particularly limited, but is, for example, 0.0% by mass or 0.001% by mass. The QI is determined by the methods described in the Examples section.

[0034] The 3% distillation temperature of the base pitch of one embodiment is preferably 340°C or more, and more preferably 380°C or more. The 3% distillation temperature of the base pitch of one embodiment is preferably 470°C or less, and more preferably 450°C or less. The upper limit values and the lower limit values can be arbitrarily combined. The preferable range is 340°C or more and 470°C or less, and more preferably 380°C or more and 450°C or less. When the 3% distillation temperature is 340°C or more, the amount of light components volatilized at a kneading temperature (for example, 150°C to 170°C) is small, so that the viscosity of the pitch during kneading hardly increases, and kneading can be carried out well. On the other hand, when the 3% distillation temperature exceeds 470°C, the softening point of the base pitch may exceed 110°C, although it depends on the raw material and heat treatment conditions of step 1. Therefore, the 3% distillation temperature is preferably 470°C or less. The 3% distillation temperature is determined by the method described in the Examples section.

(Step 3: Carbon powder mixing step)

[0035] Step 3 is a step of adding carbon powder to the base pitch obtained in step 2 and mixing them. The carbon powder used is not particularly limited as long as it improves the carbon yield without deteriorating the kneadability and formability of the obtained binder pitch. For example, carbon powder having a particle diameter of about 1 nm to 20 μm can be used. As to the above particle diameter range, the particle diameter of particles having a particle diameter of 10 nm or more means an average particle diameter (median diameter: D50) measured by the laser diffraction/scattering method, and the particle diameter of particles having a particle diameter of less than 10 nm means an arithmetic average diameter determined by the electron microscope observation. Such carbon powder includes, for example, graphite powder, such as artificial graphite powder, and natural graphite powder; coke powder, carbon black powder, and free carbon powder in coal tar, and at least one selected from the group consisting of artificial graphite powder, coke powder, and carbon black powder is preferable. The carbon powder can be used alone or as a mixture of two or more thereof. In one embodiment, the carbon powder is at least one selected from the group consisting of artificial graphite powder and carbon black powder.

[0036] The amount of carbon powder added is preferably 1.0 parts by mass or more, more preferably 3.0 parts by mass or more, and still more preferably 5.0 parts by mass or more, with respect to 100 parts by mass of the base pitch. The amount of carbon powder added is preferably 22.0 parts by mass or less, more preferably 18.0 parts by mass or less, and still more preferably 11.0 parts by mass or less, with respect to 100 parts by mass of the base pitch. The upper limit values and the lower limit values can be arbitrarily combined. The preferable range is 1.0 parts by mass or more and 22.0 parts by mass or less, more preferably 3.0 parts by mass or more and 18.0 parts by mass or less, and still more preferably 5.0 parts by mass or more and 11.0 parts by mass or less, with respect to 100 parts by mass of the base pitch. When it is within the above ranges, the obtained binder pitch has a quinoline insoluble matter of 18.0% by mass or less, although it depends on the amount of quinoline insoluble matter in the base pitch. Thus, the carbon yield can be improved without deteriorating the kneadability and the formability.

[0037] The method of mixing the base pitch and the carbon powder is not particularly limited, but a method in which the carbon powder is well dispersed in the base pitch is preferable.

[0038] Examples thereof include a method of mixing the base pitch and the carbon powder at a temperature equal to or

higher than the softening point of the base pitch. When the base pitch and the carbon powder are mixed at a temperature equal to or higher than the softening point of the base pitch, the mixing temperature is preferably 350°C or less, more preferably 250°C or less, and still more preferably 200°C or less. When the temperature is 350°C or less, it is possible to minimize the deterioration of the base pitch, which may occur during mixing, although it depends on the mixing conditions, etc. The mixing time is not particularly limited, but is, for example, 5 minutes to 24 hours. When it is within the above range, it is possible to disperse the carbon powder well in the base pitch, although it depends on the mixing conditions, etc. The mixing atmosphere is not particularly limited, and mixing can be carried out under air or under a non-oxidizing gas atmosphere. Mixing is preferably carried out under a non-oxidizing gas atmosphere from the viewpoint of minimizing the deterioration of the base pitch, which may occur during mixing. Examples of the non-oxidizing gas include nitrogen gas, argon, hydrogen gas, lower alkane gas, such as methane and ethane, and a mixed gas of these non-oxidizing gases. Among them, nitrogen gas is preferable from the viewpoint of cost and ease of handling. The mixing apparatus is not particularly limited, and for example, a heatable mixer, kneader, etc., can be used.

[0039] Examples of other mixing methods include a method in which the base pitch is dissolved in a suitable solvent and mixed with carbon powder. In this case, a step of removing the solvent by reduced-pressure distillation, etc., after mixing is necessary. Suitable solvents are not particularly limited as long as it can dissolve the base pitch well, and benzene, toluene, xylene, quinoline, pyridine, and mixtures thereof can be used. Benzene and toluene rich fractions obtained in petrochemical processes can also be utilized. Such fractions include, for example, cracked gasoline and cracked kerosene.

[0040] Cracked gasoline is a mixture composed mainly of hydrocarbons having 6 to 8 carbon atoms and produced in petrochemical processes, and is a fraction having a boiling point in the range of 65°C to 150°C at 1 atm. However, since cracked gasoline is a mixture of hydrocarbons, the number of carbon atoms and boiling point may vary to some extent.

[0041] Examples of primary components of cracked gasoline include benzene, toluene, ethylbenzene, xylene, styrene and hexane.

[0042] Cracked kerosene is as described above.

[0043] The mixing using a solvent can be carried out at room temperature or under heating conditions. When mixing is carried out at normal pressure, mixing is preferably carried out at or below the boiling point of the solvent used. When mixing is carried out at a temperature higher than or equal to the boiling point of the solvent used, mixing can be carried out under reflux conditions or under pressure using a sealed vessel. The mixing temperature is preferably 350°C or less, more preferably 250°C or less, and still more preferably 200°C or less, although it depends on the mixing conditions, etc. When the temperature is 350°C or less, it is possible to minimize the deterioration of the base pitch, which may occur during mixing, although it depends on the mixing conditions, etc. The mixing time is not particularly limited, but is, for example, 5 minutes to 24 hours. When it is within the above range, it is possible to disperse the carbon powder well in the base pitch, although it depends on the mixing conditions, etc. The mixing atmosphere is not particularly limited, and mixing can be carried out under air or under a non-oxidizing gas atmosphere. Mixing is preferably carried out under a non-oxidizing gas atmosphere from the viewpoint of minimizing the deterioration of the base pitch, which may occur during mixing. Examples of the non-oxidizing gas include nitrogen gas, argon, hydrogen gas, lower alkanes, such as methane and ethane, and a mixed gas of these non-oxidizing gases. Among them, nitrogen gas is preferable from the viewpoint of cost and ease of handling.

[0044] When the base pitch and the carbon powder are mixed using a solvent, a solvent removal step is required after step 3. The method of removing the solvent is not particularly limited, but a method capable of efficiently removing the solvent without deteriorating the base pitch is preferable. Such a solvent removal method includes, for example, distillation. The distillation method in this case may be any of atmospheric distillation, reduced-pressure distillation (vacuum distillation), or a combination of atmospheric distillation and reduced-pressure distillation, and can be appropriately selected. It is preferable that the internal temperature of a distillation apparatus not exceed 360°C. This is because, when the temperature exceeds 360°C, a reaction, such as polymerization is more likely to occur and deterioration of the base pitch may occur. Since the lower limit temperature and the pressure in the case of carrying out reduced-pressure distillation (vacuum distillation) do not affect the physical properties of the base pitch, the conditions can be appropriately selected depending on the type of the solvent used.

[0045] The total content of carbon powder in the binder pitch obtained in step 3 of one embodiment is preferably 1.0 to 18.0% by mass, more preferably 3.0 to 15.0% by mass, and still more preferably 5.0 to 10.0% by mass.

[0046] The softening point of the binder pitch obtained in step 3 of one embodiment is preferably 80°C or more, and more preferably 90°C or more. The softening point of the binder pitch obtained in step 3 of one embodiment is preferably 120°C or less, and more preferably 110°C or less. The upper limit values and the lower limit values can be arbitrarily combined. The preferable range is 80°C or more and 120°C or less, and more preferably 90°C or more and 110°C or less. When the softening point is 80°C or more and 120°C or less, the binder pitch can sufficiently soften at a kneading temperature (for example, 140°C to 180°C), and therefore favorable kneadability is obtained. The softening point is determined by the method described in the Examples section.

[0047] The quinoline insoluble matter of the binder pitch obtained in step 3 of one embodiment is preferably 18.0% by

mass or less, more preferably 15.0% by mass or less, and still more preferably 10.0% by mass or less. When it is 18.0% by mass or less, the binder pitch can sufficiently wet the surface of the needle coke in the kneading step, which is one of the manufacturing steps of a graphite electrode, and therefore, favorable formability is obtained. The quinoline insoluble matter of the binder pitch obtained in step 3 of one embodiment is preferably 1.0% by mass or more, more preferably 3.0% by mass or more, and still more preferably 5.0% by mass or more. The quinoline insoluble matter of the binder pitch includes, the carbon powder added in step 3 in addition to the quinoline insoluble matter contained in the base pitch. The quinoline insoluble matter is determined by the method described in the Examples section.

<Manufacturing process of graphite electrode>

[0048] The carbon materials refer to various types of formed carbon materials, such as graphitic tubes, graphitic crucibles, graphitic boats, and graphite electrodes. Hereinafter, a general manufacturing process of the graphite electrode will be described.

1. Kneading step

[0049] A step of mixing needle coke and a binder pitch together and kneading them

2. Forming step

[0050] A step of forming the kneaded product to obtain a formed product having a predetermined size and shape

3. Baking step

[0051] A step of baking the formed body to obtain a baked body

4. Impregnation step

[0052] A step of filling the baked body with an impregnation pitch

5. Re-baking step

[0053] A step of re-baking the baked body filled with the impregnation pitch to obtain a re-baked body

6. Graphitization step

[0054] A step of graphitizing the re-baked body to obtain a graphitized body

7. Processing step

[0055] A step of forming the graphitized body into a predetermined shape by cutting or the like to form a graphite electrode

1. Kneading step

[0056] Needle coke, which is pulverized, classified, and blended in a predetermined grain ratio, and a binder pitch are mixed together and kneaded. The blending amount of the binder pitch varies, depending on the kneading method and the forming method, but is generally about 20 parts by mass to 30 parts by mass with respect to 100 parts by mass of the needle coke.

[0057] The kneaded product may include a puffing inhibitor, such as iron oxide.

[0058] A commercially available mixing apparatus or kneading apparatus can be used for mixing and kneading. Specific examples thereof include a mixing apparatus and a kneading apparatus, such as a mixer and a kneader. The kneading temperature varies, depending on the binder pitch used, but is generally about 140°C to 180°C. After kneading, the kneaded product is cooled to a temperature suitable for subsequent forming (e.g., 100°C to 130°C).

[0059] The softening point of the binder pitch used varies, depending on the type of carbon material to be produced, producing method, etc., but is preferably 80°C to 120°C. The fixed carbon content is preferably 45.0% by mass or more, and more preferably 50.0% by mass or more.

2. Forming step

[0060] The kneaded product is formed to obtain a formed product having a predetermined size and shape. The forming method can be appropriately selected from extrusion, molding, etc., depending on the target carbon material. When the target carbon material is a graphite electrode, extrusion into a cylindrical shape is common.

3. Baking step

[0061] The formed body of the previous step is heated and baked at 700°C to 1000°C to obtain a baked body. The baking step is preferably carried out in a combustion exhaust gas non-oxidizing atmosphere. The formed body softens at the initial stage of a temperature rise, a large amount of decomposition gas is generated by thermal decomposition and polycondensation of the binder pitch at 200°C to 500°C, and the formation of pores and volume shrinkage occur. The binder pitch carbonizes at 500°C to 600°C. The baking step often requires about one month, including cooling.

4. Impregnation step

[0062] In the baking step, the binder pitch generally loses 35% to 45% of its mass as a volatile matter. At this time, a large number of pores are generated in the baked body. The impregnation step is to fill the pores with the impregnation pitch. The impregnation is carried out, for example, by placing the baked body in an autoclave, degassing under reduced pressure, injecting a molten impregnation pitch, and injecting the impregnation pitch into the pores at a gas pressure of around 1 MPa at about 200°C.

[0063] The softening point of the impregnation pitch used varies, depending on the type of carbon material to be produced, producing method, etc., but is preferably 80°C to 120°C. The fixed carbon content is preferably 45.0% by mass or more, and more preferably 50.0% by mass or more.

5. Re-baking step

[0064] The baked body filled with the impregnation pitch is re-baked to obtain a re-baked body. The re-baking can also be carried out under the same conditions as in the baking step. The impregnation step and the re-baking step may be repeated, if necessary.

6. Graphitization step

[0065] The re-baked body is placed in a furnace surrounded by an insulating material (Acheson furnace, LWG furnace, etc.), and subjected to a heat treatment by resistance heat generation of packing coke or the re-baked body by energization. The temperature of graphitization is 2000°C to 3000°C. This temperature is necessary to convert amorphous carbon in the re-baked body into crystalline graphite. In order to convert the re-baked body into graphitized body, the heat treatment is preferably carried out for several days.

7. Processing step

[0066] The graphitized body is formed into a graphite electrode product having a predetermined shape by machining, such as cutting. The density (bulk density) of the graphite electrode varies, depending on the electric furnace installation used and the operating conditions of the electric furnace, but preferably is 1.5 g/cm³ to 1.9 g/cm³.

EXAMPLES

[0067] The present invention will be further described with reference to Examples, and Comparative Examples below, but these Examples merely illustrate examples of the present invention, and the present invention is not limited to these Examples.

<Method for measuring softening point (SP)>

[0068] The softening point was measured in accordance with JIS K 2425:2006 "8. Measuring method for softening point of tar pitch (ring and ball method)" of the "Test method of creosote oil, prepared tar and tar pitch".

<Method for measuring fixed carbon (FC) content>

[0069] Fixed carbon content was measured in accordance with JIS K 2425:2006 "11. Method of determination of fixed carbon content" of the "Test method of creosote oil, prepared tar and tar pitch".

<Method for measuring toluene insoluble matter (TI)>

[0070] Toluene insoluble matter (TI) was measured in accordance with the filtration method described in JIS K 2425:2006 "14.2 Method of determination of toluene-insoluble content in prepared tar and tar pitch" of the "Test method of creosote oil, prepared tar and tar pitch".

<Method for measuring quinoline insoluble matter (QI)>

[0071] Quinoline insoluble matter (QI) was measured in accordance with the filtration method described in JIS K 2425:2006 "15. Method of determination of quinoline-insoluble content in tar pitch" of the "Test method of creosote oil, prepared tar and tar pitch".

<Method for measuring distillation characteristics of base pitch>

[0072] The initial boiling point and 3% distillation temperature of the base pitch were measured in accordance with "6. Reduced-pressure method" described in JIS K 2254:2018 "Petroleum products-Determination of distillation characteristics".

<Method for measuring true density of pitch>

[0073] The true density of the pitch was measured by the constant volume expansion method using AccuPyc II 1340 (Micromeritics Instrument Corporation). The measurement was carried out at 25°C using helium as the displacement gas.

<Electrode evaluation>

[0074] A binder pitch and needle coke were mixed (needle coke:binder pitch = 8:2, mass ratio) using a laboratory kneader (Toshin Co., Ltd., TDR200-3 type), and formed into a shape of an electrode piece (cylindrical; 50 mmΦ × 35 mm) by molding to prepare a formed body. The formed body was baked at about 1000°C to produce a baked body. The density of the formed body and the baked body was measured in accordance with JIS R 7222:2017 "Test methods for physical properties of graphite materials 7. Measuring method for bulk density". The carbon yield was calculated using formula (1).

$$\text{Carbon yield (\%)} = \frac{W_3 - W_2}{W_1} \times 100 \quad (1)$$

W_1 : mass of binder pitch used for preparing formed body

W_2 : mass of needle coke used for preparing formed body

W_3 : mass of baked body

<Carbon powder>

[0075] As the artificial graphite powder, artificial graphite fine powder (UF-G5) (Resonac Corporation, particle diameter: 3 μm) was used. As the carbon black powder, carbon black (MA230) (Mitsubishi Chemical Corporation, particle diameter: 30 nm) was used.

<Method for mixing carbon powder and base pitch>

[0076] A base pitch was placed in a beaker and heated to a predetermined temperature in an oil bath to dissolve the base pitch. Carbon powder was added thereto and the mixture was mixed using a three-one motor to prepare a binder pitch. The type of carbon powder used, the amount of carbon powder added, the mixing temperature, and the mixing time are as described in the section of Examples and Comparative Examples.

<Stability evaluation at kneading temperature>

[0077] A paste prepared by mixing the binder pitch of Examples or Comparative Examples and needle coke at 150°C for 5 minutes (needle coke: binder pitch = 3:7, mass ratio) was evaluated as a measurement sample. The measurement sample was measured at 170°C for 1 hour at a shear rate of 10 s⁻¹, and the change with time in the viscosity was recorded. MCR72 (Anton Paar GmbH) was used to measure the viscosity. The viscosity increase rate (%) was calculated using formula (2) on the basis of the viscosity at 10 minutes after the start of measurement. When the viscosity increase rate at 60 minutes after the start of measurement is 1.0% or less, it was determined to be stable at the kneading temperature (here, 170°C). When the viscosity increase rate at 60 minutes after the start of measurement is 1.0% or less, it was determined to be "good", and when the viscosity increase rate exceeds 1.0%, it was determined to be "poor". The results are summarized in Table 1. The change with time in the viscosity increase rate is shown in FIG. 2.

$$\text{Viscosity increase rate (\%)} = \frac{\eta_{X\min} - \eta_{10\min}}{\eta_{10\min}} \times 100 \quad (2)$$

$\eta_{10\min}$: viscosity at 10 minutes after start of measurement

$\eta_{X\min}$: viscosity at x minutes after start of measurement

<Ethylene bottom oil heavy fraction and light fraction>

[0078] Using 894 kg of ethylene bottom oil (5% by mass distillation temperature: 196°C, 90% by mass distillation temperature: 575°C) as a raw material, distillation refinement was carried out at a pot temperature of 101°C and an operating pressure of 533 to 1,067 PaA using distillation equipment having a theoretical plate number of 15 (Sulzer packing) to obtain 544 kg of an ethylene bottom oil heavy fraction as a bottom liquid. The initial boiling point of the obtained ethylene bottom oil heavy fraction was 218°C. The components obtained as distillate were used as the ethylene bottom oil light fraction.

<Method for measuring raw material composition (boiling range)>

[0079] The raw material composition (boiling range) of the ethylene bottom oil and the ethylene bottom oil light fraction as the raw material was measured in accordance with the method described in ASTM D7500-15 "Standard Test Method for Determination of Boiling Range Distribution of Distillates and Lubricating Base Oils-in Boiling Range from 100°C to 735°C by Gas Chromatography". AC SIMDIS Analyzer (PAC L.P.) was used for the measurement.

Example 1

[0080] 3,000 g of the ethylene bottom oil light fraction was introduced into a SUS autoclave with a capacity of 6.0 L. The autoclave was sealed under a nitrogen gas atmosphere, the inside of the vessel was heated to 430°C at a rate of 4°C/min while stirring, and a heat treatment was carried out. After 6 hours had elapsed since the temperature reached 430°C, the product was allowed to cool to room temperature, and the heat-treated product was discharged. The heat-treated product was distilled under reduced pressure using a reduced pressure distillation apparatus to distill off the low boiling point components, whereby 720 g (yield: 24%) of base pitch was obtained as a high boiling point component. The physical properties of the obtained base pitch are as shown in Table 1. 9.6 g of the artificial graphite powder was added to 110.4 g of the base pitch, and the mixture was heated and mixed at 140°C for 30 minutes using a three-one motor to prepare 120 g of binder pitch, and various evaluations were carried out.

Example 2

[0081] 6 g of the carbon black powder was added to 114 g of the base pitch obtained in Example 1, and the mixture was heated and mixed at 140°C for 30 minutes using a three-one motor to prepare 120 g of binder pitch, and various evaluations were carried out.

Comparative Example 1

[0082] 550 g of the ethylene bottom oil was introduced into a SUS autoclave with a capacity of 1.0 L. The autoclave was sealed under a nitrogen gas atmosphere, the inside of the vessel was heated to 380°C at a rate of 4°C/min while stirring,

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and a heat treatment was carried out. After 36 hours had elapsed since the temperature reached 380°C, the product was allowed to cool to room temperature, and the heat-treated product was discharged. The heat-treated product was distilled under reduced pressure using a reduced pressure distillation apparatus to distill off the low boiling point components, whereby 226 g (yield: 41%) of pitch was obtained as a high boiling point component. Physical properties of the obtained pitch are as shown in Table 1. 9.6 g of the artificial graphite powder was added to 110.4 g of the pitch, and the mixture was heated and mixed at 140°C for 30 minutes to obtain 120 g of pitch. Various evaluations were carried out using the obtained pitch as a binder pitch.

Comparative Example 2

[0083] The ethylene bottom oil was distilled under reduced pressure without a heat treatment to obtain pitch. Physical properties of the obtained pitch are as shown in Table 1. 9.6 g of the artificial graphite powder was added to 110.4 g of the pitch, and the mixture was heated and mixed at 140°C for 30 minutes to obtain 120 g of pitch. Various evaluations were carried out using the obtained pitch as a binder pitch.

Comparative Example 3

[0084] Various evaluations were carried out using the base pitch obtained in Example 1 as a binder pitch.

Reference Example 1

[0085] The data of commercially available coal tar-based binder pitch are presented.

Table 1

			Ex. 1	Ex. 2	Comp. Ex. 1
Raw material	Type of raw material		Ethylene bottom oil light fraction	Ethylene bottom oil light fraction	Ethylene bottom oil
	Raw material composition/ % by mass (boiling range)	<150°C	0	0	0
		150°C≤b.p.<450°C	100	100	71
		450°C≤b.p.<550°C	0	0	15
		≥550°C	0	0	14
Base pitch preparation conditions	Heat treatment conditions	Temperature/ °C	430	430	380
		Time/ hrs	6	6	36
	Distillation conditions	Distillation end point (in terms of normal pressure)/ °C	385	385	320
Physical properties of base pitch	Softening point/ °C		91	91	87
	Fixed carbon content/ % by mass		51.1	51.1	50.8
	Toluene insoluble matter/ % by mass		3.0	3.0	17.5
	Quinoline insoluble matter/ % by mass		0.0	0.0	0.0
	Initial boiling point/ °C		372	372	311
	3% distillation temperature/ °C		399	399	333
Carbon powder addition conditions	Type		artificial graphite powder	carbon black powder	artificial graphite powder
	Amount added with respect to 100 parts by mass of base pitch/ parts by mass		8.7	5.3	8.7

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(continued)

			Ex. 1	Ex. 2	Comp. Ex. 1
Physical properties of binder pitch	Softening point/ °C		93	94	90
	Fixed carbon content/ % by mass		55.3	53.4	54.2
	Quinoline insoluble matter/ % by mass		8.0	5.0	8.0
	True density/ g·cm ⁻³		1.250	1.234	1.254
	Stability at kneading temperature (170°C)		good	good	poor
		Viscosity increase rate/ %	<0.1	<0.1	1.5
Electrode evaluation	Formed body density/ g·cm ⁻³		1.850	1.857	1.771
	Carbon yield/ % by mass		74.1	61.4	66.5
	Baked body density/ g·cm ⁻³		1.616	1.584	1.587

(Continuation of Table 1)

[0086]

			Comp. Ex. 2	Comp. Ex. 3	Ref. Ex.
Raw material	Type of raw material		Ethylene bot- tom oil	Ethylene bottom oil light fraction	Coal tar pitch
	Raw material composition/ % by mass (boiling range)	<150°C	0	0	-
		150°C≤b.p.<450°C	71	100	-
		450°C≤b.p.<550°C	15	0	-
		≥550°C	14	0	-
Base pitch preparation conditions	Heat treat- ment condi- tions	Temperature/ °C	-	430	-
		Time/ hrs	-	6	-
	Distillation conditions	Distillation end point (in terms of normal pressure)/ °C	270	385	-
Physical properties of base pitch	Softening point/ °C		116	91	-
	Fixed carbon content/ % by mass		27.2	51.1	-
	Toluene insoluble matter/ % by mass		0.0	3.0	-
	Quinoline insoluble matter/ % by mass		0.0	0.0	-
	Initial boiling point/ °C		245	372	-
	3% distillation temperature/ °C		279	399	-
Carbon powder ad- dition condi- tions	Type		artificial gra- phite powder	-	-
	Amount added with respect to 100 parts by mass of base pitch/ parts by mass		8.7	-	-
Physical propert i es of binder pitch	Softening point/ °C		117	91	90-100
	Fixed carbon content/ % by mass		33.5	51.1	50-60
	Quinoline insoluble matter/ % by mass		8.0	0.0	5-10
	True density/ g·cm ⁻³		1.200	1.214	-
	Stability at kneading temperature (170°C)		poor	good	good
		Viscosity increase rate/ %	3.3	0.3	0.6

(continued)

		Comp. Ex. 2	Comp. Ex. 3	Ref. Ex.
5	Elect rode evaluation	Formed body density/ g·cm ⁻³	1.821	1.847
		Carbon yield/ % by mass	38.9	58.4
		Baked body density/ g·cm ⁻³	1.433	1.548

[0087] From the comparison of the electrode evaluation results of Example 1, Example 2, and Comparative Example 3, it can be seen that the carbon yield improved by the addition of carbon powder, and the density of the obtained baked body is also improved. In addition, from the comparison between Example 1 and Comparative Example 1, it can be seen that even when the same carbon powder is used, when the physical properties of the base pitch are not appropriate, the effect cannot be sufficiently obtained. That is, the binder pitch of Comparative Example 1 has the same fixed carbon content and true density as those of Example 1, but the initial boiling point of the base pitch is low. Therefore, the stability at the kneading temperature is low, and the viscosity increases during kneading (see FIG. 2). As a result, since the kneadability and the formability are lowered, and therefore the density of the formed body is relatively low, and the carbon yield and the density of the baked body are also low. In the base pitch of Comparative Example 2, since the softening point, the fixed carbon amount, and the initial boiling point are not appropriate, the stability during kneading is poor, and the carbon yield and the density of the baked body are also significantly low. From the above, it is clear that it is important to add carbon powder to a base pitch having an appropriate softening point, fixed carbon content, initial boiling point, and quinoline insoluble matter (QI).

Claims

- A method for producing a binder pitch for a carbon material, comprising heat-treating a petroleum-based heavy oil (step 1);

 distilling the heat-treated product obtained in step 1 to obtain a base pitch having a softening point of 60°C or more and 110°C or less, a fixed carbon content of 50.0% by mass or more, an initial boiling point of 320°C or more and 450°C or less, and a quinoline insoluble matter (QI) of 1.0% by mass or less as a high boiling point component (step 2);
 adding carbon powder to the base pitch obtained in step 2 and mixing them (step 3).
- The method for producing a binder pitch for a carbon material according to claim 1, wherein a 3% distillation temperature of the base pitch is 340°C or more and 470°C or less.
- The method for producing a binder pitch for a carbon material according to claim 1 or 2, wherein the petroleum-based heavy oil is an ethylene bottom oil light fraction.
- The method for producing a binder pitch for a carbon material according to claim 1 or 2, wherein the carbon powder is at least one selected from the group consisting of graphite powder, coke powder, carbon black powder, and free carbon powder in coal tar.
- The method for producing a binder pitch for a carbon material according to claim 1 or 2, wherein an amount of the carbon powder added is 1.0 parts by mass or more and 22.0 parts by mass or less with respect to 100 parts by mass of the base pitch.
- The method for producing a binder pitch for a carbon material according to claim 1 or 2, wherein the binder pitch for a carbon material obtained in step 3 has a softening point of 80°C or more and 120°C or less, and a quinoline insoluble matter of 18.0% by mass or less.
- The method for producing a binder pitch for a carbon material according to claim 1 or 2, wherein the carbon material is a graphite electrode.

Fig. 1

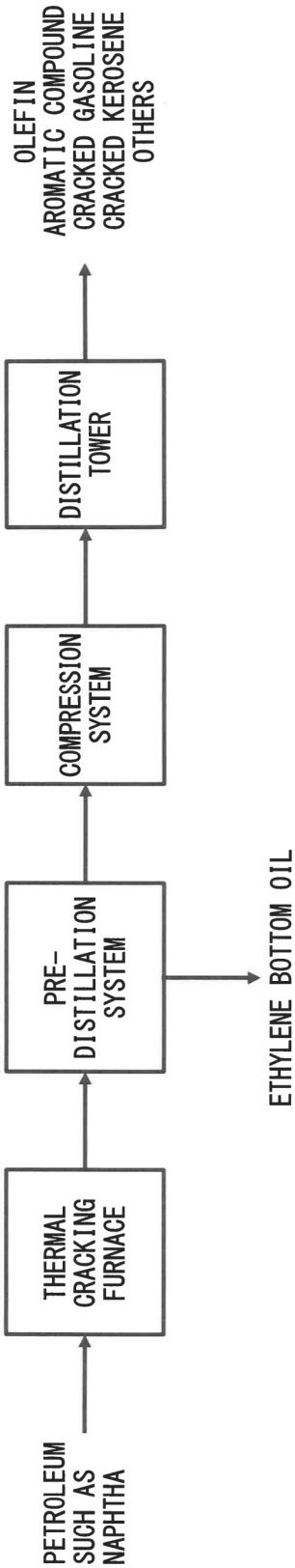
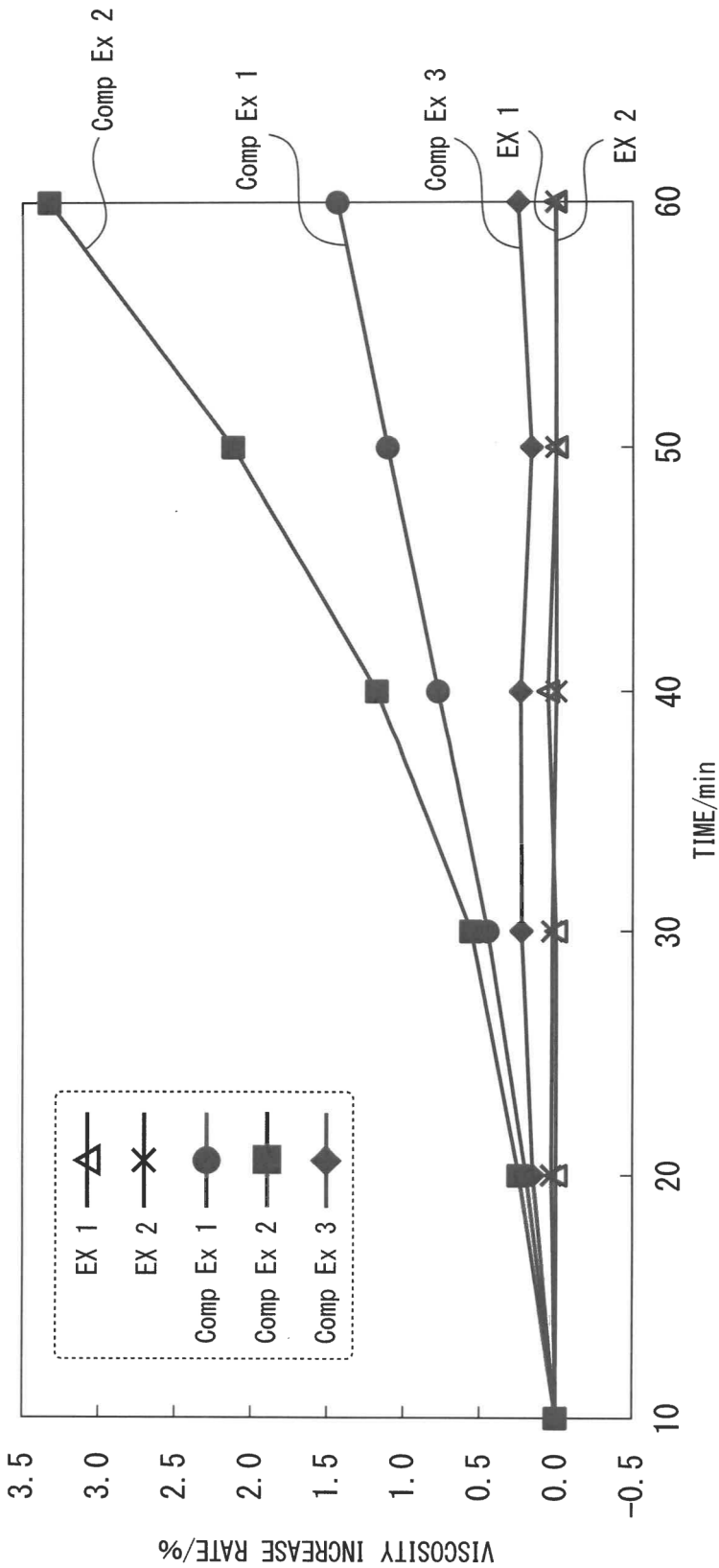


Fig. 2



INTERNATIONAL SEARCH REPORT

International application No.

PCT/JP2024/015540

A. CLASSIFICATION OF SUBJECT MATTER

C10C 3/02(2006.01)i

FI: C10C3/02 E

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

C10C3/02

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Published examined utility model applications of Japan 1922-1996

Published unexamined utility model applications of Japan 1971-2024

Registered utility model specifications of Japan 1996-2024

Published registered utility model applications of Japan 1994-2024

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	WO 2022/049953 A1 (SHOWA DENKO K.K.) 10 March 2022 (2022-03-10) examples 1-2, 4-8, 10, table 1	1-7
Y	JP 5-279669 A (MITSUBISHI KASEI CORP.) 26 October 1993 (1993-10-26) claim 1	1-7
Y	JP 5-279667 A (MITSUBISHI KASEI CORP.) 26 October 1993 (1993-10-26) claim 1	1-7
Y	JP 2-258892 A (CONOCO INC.) 19 October 1990 (1990-10-19) claim 1	1-7
A	JP 56-79190 A (NIPPON CARBON CO., LTD.) 29 June 1981 (1981-06-29)	1-7

☐ Further documents are listed in the continuation of Box C.☒ See patent family annex.

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Date of the actual completion of the international search

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INTERNATIONAL SEARCH REPORT
Information on patent family members

International application No.
PCT/JP2024/015540

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Patent document cited in search report	Publication date (day/month/year)	Patent family member(s)	Publication date (day/month/year)
WO 2022/049953 A1	10 March 2022	US 2023/0303933 A1 examples 1-2, 4-8, 10, table 1 EP 4209569 A1 CN 116096839 A	
JP 5-279669 A	26 October 1993	(Family: none)	
JP 5-279667 A	26 October 1993	(Family: none)	
JP 2-258892 A	19 October 1990	US 4959139 A claim 1 EP 378326 A2 CA 1333374 A1	
JP 56-79190 A	29 June 1981	(Family: none)	

REFERENCES CITED IN THE DESCRIPTION

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Patent documents cited in the description

- US 6352637 B2 [0006]
- JP S60179493 A [0028]
- JP S60240790 A [0028]